Reactions of a tungsten alkylidyne complex with mono-dentate phosphines: Thermodynamic and theoretical studies

Ping Chen a, Brenda A. Dougan b, Xinhao Zhang a,*, Yun-Dong Wu a,*, Zi-Ling Xue b,∗

a Lab of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, PR China
b Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

A R T I C L E   I N F O
Article history:
Available online xxxx

Dedicated to the memory of Michelle Millar, a scientist and teacher who gave so much to the chemistry communities.

Keywords:
Alkylidyne
Alkylidene
Phosphine adduct
Equilibrium
DFT calculations
α-H abstraction

A B S T R A C T
Addition of mono-dentate phosphines PMe3 and PMe2Ph to the W(VI) alkyl alkylidyne complex W(CH2CMe3)2(═CHSiMe3) (1) is reversible, each reaching equilibrium. Thermodynamic studies of the equilibria have been conducted, giving ΔF° = −10.0(1.1) kcal mol⁻¹ and ΔS° = −23(4) eu for the addition of PMe3 and ΔF° = −3.0 (0.7) kcal mol⁻¹ and ΔS° = −6 (3) eu for the addition of PMe2Ph, indicating that the addition is exothermic. The experimental measurement allows a benchmarking study to select a proper DFT method to describe the current system. Of the DFT methods tested, M06 has demonstrated superior performance in calculating binding energy of a bimolecular reaction. The calculated reaction pathways show that W(CH2CMe3)2(═CHSiMe3) (1) reacts with PR3 to form W(CH2SiMe3)2(═CHSiMe3)(PR3) (PR3 = PMe3, 3a; PMe2Ph, 3b), and the adduct then undergoes α-H migration to form W(CH2SiMe3)2(═CHSiMe3)(PR3)2 (4a, 4b). 4a and 4b are found to be thermodynamically and kinetically stable intermediates. The calculations also suggest a pathway in the formation of the alkyl alkylidyne alkylidyne complex W(CH2SiMe3)2(═CHSiMe3)(DMPE)2 (5a).

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction
High-oxidation-state metal alkylidyne and alkylidyne complexes containing M≡C and M≡C bonds, respectively, often demonstrate unique chemistry and have been extensively studied [1–4]. The alkylidyne and alkylidyne complexes usually contain ligands such as neopentyl (═CH2CMe3) and trimethylsilylmethyl ligands (═CH2SiMe3) that are free of α-H atoms [1–4]. Complexes containing a –CH2SiMe3 ligand with a β-Si atom often show properties different from those containing its neopentyl –CH2CMe3 analog. For example, Clark and Schrock reported that the reactions of W(CH2CMe3)2(═CCMe3) with phosphines PMe3 and Me2PCH2CH2PMe3 (DMPE) give the bis-phosphine/chelating phosphine products W(CH2CMe3)(═CHCMe3)(═CCMe3)(PMe3)2 (1) and W(CH2CMe3)(═CHCMe3)(DMPE) through α-H abstraction [3b]. The structure of the latter was determined by Churchill and Youngs [5]. In comparison, we have found that W(CH2SiMe3)2(═CHSiMe3) (2) reacts with PMe3, PMe2Ph, and DMPE, forming phosphine adducts W(CH2SiMe3)2(═CHSiMe3)(PR3) (PR3 = PMe3, 3a; PMe2Ph, 3b) (Scheme 1) and W(CH2SiMe3)2(═CHSiMe3)(DMPE)2 (3e) (Scheme 2) containing one free PMe3 group [6]. These adducts undergo α-H migration to form their bis-alkylidyne tautomers W(CH2SiMe3)2(═CHSiMe3)(PR3)2 (4a, 4b) and W(CH2SiMe3)2(═CHSiMe3)2(DMPE-P) (4e). The tautomeric mixtures are in equilibria, and undergo α-H abstraction to eliminate SiMe3 to form, by reacting with free PR3 and the free PMe2Ph group in DMPE ligand, W(CH2SiMe3)2(═CHSiMe3)(DMPE)2 (5a-b, 6a-b) (Scheme 1) and W(CH2SiMe3)2(═CHSiMe3)(DMPE) (5e, 6e) (Scheme 2), respectively [6].

Another example of the difference between –CH2SiMe3 and –CH2CMe3 ligands is the reactions shown in Scheme 3 [7], Ta(═CHR)2(CH2SiMe3)(PMe3)2 (R = SiMe3, CMe3) reacts with silanes to give metallocyclic products. In comparison, its neopentyl analog, Ta(═CHCMe3)2(CH2CMe3)(PMe3)2, forms unknown species with the silanes.

We have been interested in the tautomeration between alkyl alkylidylenes (3a, 3b, 3e) and bis-alkylidylenes (4a, 4b, 4e) in Schemes 1 and 2 because these were among the few reported direct observation of exchanges through α-H migration [1j,m], although such exchanges had been implicated in several systems [8–12]. The tautomeration of silyl alkylidyne (Me3CCH2)W(═CCMe3)(SiBuPh2) with bis-alkylidyne (Me3CCH2)W(═CHCMe3)(SiBuPh2) was, to our knowledge, the first directly observed exchange [13].

In the current work, we studied the thermodynamics of the reversible addition of PMe3 and PMe2Ph to 1 forming 3a and 3b, respectively, in order to probe the unusual chemistry of 1 in detail. Density functional theory (DFT) studies have been performed to: (1) understand the thermodynamics and kinetics of the transformation from 1 to 4; (2) explain why 4 is a relatively stable intermediate along the pathway to 5.

* Corresponding authors.
E-mail addresses: zhangxh@pku.edu.cn (X. Zhang), chdywu@ust.hk (Y.-D. Wu), xue@ion.chem.utk.edu (Z.-L. Xue).
2. Material, methods and computational details

All manipulations were performed under a dry nitrogen atmosphere with the use of either a dry box or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. Toluene-$d_8$ was dried over activated molecular sieves and stored under N$_2$. $\text{WCl}_6$ was freshly sublimed under vacuum. $\text{W}($MeO$)_3$WCl$_3$ and six equivalents of Me$_3$SiCH$_2$MgCl by a procedure similar to that used in the preparation of $\text{W}($MeO$)_3$WCl$_3$($\text{CH}_2$CMe$_3$) [14]. $^1$H NMR spectra were recorded on a Bruker AMX-400 spectrometer.

For the thermodynamic studies, the equilibrium constants $K_{eq}$ were obtained from at least five separate experiments at a given temperature, and their averages are listed in Table 1. The maximum random uncertainty in the equilibrium constants were combined with the estimated systematic uncertainty of ca. 5%. The total uncertainties in the equilibrium constants were used in the $\ln K_{eq}$ versus $1000/T$ plot in Fig. 1 and the error propagation calculations. The estimated uncertainty in the temperature measurements for an NMR probe was 1 K. The enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) changes were calculated from an unweighted non-linear least-squares procedure. The uncertainties in $\Delta H^\circ$ and $\Delta S^\circ$ were computed from the following error propagation formulas, which were derived from $-RT \ln K_{eq} = \Delta H^\circ - T \Delta S^\circ$ [13].

$$
(\sigma_{\Delta H})^2 = \frac{R^2(T_{max}^4 - T_{min}^4)}{(T_{max}^4 - T_{min}^4)} \left[ \ln \left( \frac{K_{eq(max)}}{K_{eq(min)}} \right) \right]^2 \frac{(\sigma T)^2}{T} + \frac{2R^2(T_{max}^4 - T_{min}^4)}{(T_{max}^4 - T_{min}^4)} \left( \frac{\sigma K_{eq}}{K_{eq}} \right)^2 \tag{1}
$$

Scheme 1. Reactions of mono-dentate phosphines with 1 [6a,b,d].

Scheme 2. Reaction of the bisdentate phosphine DMPE with 1 [6c].

Scheme 3. Reactions of PhR$^0$SiH$_2$ (R$^0$ = Me, Ph, CH$_2$SiH$_2$Ph) with phosphine alkylidene complexes.
Table 1
Equilibrium constants ($K_{eq1}$ and $K_{eq1}'$) of $1 + PR_3 = 3a/4a$ and $3b/4b$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_{eq1}$ for $1 + PMe_3 = 3a/4a$</th>
<th>$K_{eq1}'$ for $1 + PMe_2Ph = 3b/4b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>263(1)</td>
<td>10.8(0.4) x 10^2</td>
<td>16.4(1.5)</td>
</tr>
<tr>
<td>273(1)</td>
<td>7.1(0.8) x 10^2</td>
<td>12.0(1.7)</td>
</tr>
<tr>
<td>283(1)</td>
<td>5.3(0.3) x 10^2</td>
<td>10.3(0.4)</td>
</tr>
<tr>
<td>293(1)</td>
<td>3.6(0.3) x 10^2</td>
<td>8.8(0.6)</td>
</tr>
<tr>
<td>303(1)</td>
<td>2.23(0.03) x 10^2</td>
<td>5.3(0.3)</td>
</tr>
</tbody>
</table>

a Solvent: toluene-$d_8$

b The relatively small temperature ranges of 30–40 K for the exchanges, $1 + PMe_3 = 3a/4a$ and $1 + PMe_2Ph = 3b/4b$, respectively, lead to relatively large uncertainties in thermodynamic ($\Delta H$ and $\Delta S$) as the error calculations in the experimental section show.

c For the equilibrium involving PMe_3 and $3a/4a$, the largest random uncertainty is $r_{K_{eq1}} = 0.84/7.1 = 12%$. The total uncertainty $r_{K_{eq1}}$ of 13% was calculated from $r_{K_{eq1}} (ran) = 12%$ and the estimated systematic uncertainty $r_{K_{eq1}} (sys)/K_{eq1} = 5%$. The total uncertainty $r_{K_{eq1}}$ of 15% was calculated from $r_{K_{eq1}} (ran)/K_{eq1} = 14%$ and the estimated systematic uncertainty $r_{K_{eq1}} (sys)/K_{eq1} = 5%$.

d For the equilibrium involving PMe_2Ph and $3b/4b$, the largest random uncertainty is $r_{K_{eq1}} (ran) = 1.7/12 = 14%$. The total uncertainty $r_{K_{eq1}}$ of 15% was calculated from $r_{K_{eq1}} (ran)/K_{eq1} = 14%$ and the estimated systematic uncertainty $r_{K_{eq1}} (sys)/K_{eq1} = 5%$.
Table 2
Relative enthalpies (kcal mol\(^{-1}\)) involved in the equilibrium \(1 + \text{PMe}_3 \rightarrow 4a\).

<table>
<thead>
<tr>
<th>Methods</th>
<th>1</th>
<th>2</th>
<th>3a</th>
<th>4a</th>
<th>(\Delta H_1)</th>
<th>(\Delta H_2 = H_{\text{mp}}(4a) - H_{\text{mp}}(3a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-phase</td>
<td>B3LYP</td>
<td>0.0</td>
<td>7.4</td>
<td>5.6</td>
<td>2.7</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>M06</td>
<td>0.0</td>
<td>9.2</td>
<td>-9.4</td>
<td>-12.1</td>
<td>-2.7</td>
</tr>
<tr>
<td></td>
<td>BP86</td>
<td>0.0</td>
<td>5.8</td>
<td>2.6</td>
<td>-2.6</td>
<td>-5.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>B3LYP</td>
<td>0.0</td>
<td>8.9</td>
<td>9.7</td>
<td>6.7</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>M06</td>
<td>0.0</td>
<td>7.3</td>
<td>-5.8</td>
<td>-8.8</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>BP86</td>
<td>0.0</td>
<td>9.5</td>
<td>6.6</td>
<td>2.1</td>
<td>-4.5</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-10.0</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

Table 3
Entropy (eu) involved in the equilibrium \(1 + \text{PMe}_3 \rightarrow 4a\).

<table>
<thead>
<tr>
<th>Entropy</th>
<th>1</th>
<th>2</th>
<th>3a</th>
<th>4a</th>
<th>(\Delta S_1 = S(4a) - [S(1) + S(\text{PMe}_3)])</th>
<th>(\Delta S_2 = S(4a) - S(3a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-phase</td>
<td>241.1</td>
<td>77.8</td>
<td>267.2</td>
<td>262.8</td>
<td>-56.1</td>
<td>-4.4</td>
</tr>
<tr>
<td></td>
<td>44.7</td>
<td>38.9</td>
<td>45.1</td>
<td>45.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>35.9</td>
<td>25.4</td>
<td>36.4</td>
<td>36.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>160.5</td>
<td>13.5</td>
<td>185.7</td>
<td>181.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>227.2</td>
<td>77.2</td>
<td>258.7</td>
<td>259.4</td>
<td>-45.0</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>44.7</td>
<td>38.9</td>
<td>45.1</td>
<td>45.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>35.7</td>
<td>25.3</td>
<td>36.5</td>
<td>36.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>146.7</td>
<td>13.0</td>
<td>177.2</td>
<td>177.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>199.0</td>
<td>54.7</td>
<td>230.2</td>
<td>230.9</td>
<td>-22.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-23(4)</td>
<td>-1.5(1.7)</td>
</tr>
</tbody>
</table>

* \(S_{\text{total}} = S_{\text{vibr.}} + S_{\text{rot.}} + S_{\text{trans.}}\)
* \(S_{\text{corr}} = 0.65 \times (S_{\text{vibr.}} + S_{\text{rot.}}) + S_{\text{trans.}}\)

Table 4
Reaction enthalpies (kcal mol\(^{-1}\)), entropies (eu) and Gibbs free energies (kcal mol\(^{-1}\)) for the reaction \(1 + \text{PMe}_3 \rightarrow 4\) and W-P distance of 4 (in Å).

<table>
<thead>
<tr>
<th></th>
<th>(\Delta H_1)</th>
<th>(\Delta S_1)</th>
<th>(\Delta G_1)</th>
<th>W-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PMe}_3) (4a)</td>
<td>-8.8/J-10.0</td>
<td>-22.8/J-23</td>
<td>-2.0/J-3.1</td>
<td>2.597/2.514</td>
</tr>
<tr>
<td>(\text{PMe}_3) (4b)</td>
<td>-8.9/J-3.0</td>
<td>-28.6/J-6</td>
<td>-0.4/J-1.2</td>
<td>2.669</td>
</tr>
<tr>
<td>(\text{PPh}_3) (4c)</td>
<td>-7.4/J-1.3</td>
<td>-29.7/J-7.5</td>
<td>2.730/J-9.3</td>
<td></td>
</tr>
<tr>
<td>(\text{PCy}_3) (4d)</td>
<td>-1.3/J-1.3</td>
<td>-29.4/J-2.8</td>
<td>2.861/J-2.7</td>
<td></td>
</tr>
</tbody>
</table>

\(\sigma \Delta S = (\sigma \Delta S)^2 = \frac{2R^2(T_{\text{min}}^2 - T_{\text{max}}^2)}{(T_{\text{max}} - T_{\text{min}})^2} \left[ \ln \left( \frac{K_{\text{eq1}}(\text{max})}{K_{\text{eq1}}(\text{min})} \right)^2 \right] \frac{\sigma T}{T} \)

\(T_{\text{min}}\) and \(T_{\text{max}}\) are the minimum and maximum temperatures in the current studies; \(T\) is the mean temperature in the current studies. \(K_{\text{eq1}}(\text{min})\) and \(K_{\text{eq1}}(\text{max})\) are the minimum and maximum equilibrium constants, respectively. \(\sigma K_{\text{eq1}}/K_{\text{eq1}}\) is given in Table 1. Similar calculations were performed for \(K_{\text{eq1}}\).

![Fig. 2. Energy decomposition analysis of the binding complex 3a and 4a (energies in kcal mol\(^{-1}\)).](image-url)
2.1. Thermodynamic study of the equilibrium between $\text{W(CH}_2\text{SiMe}_3)_3(\equiv\text{CSiMe}_3)$ (1), PMe$_3$ and the $3a = 4a$ tautomeric mixture

At least five experiments were conducted. A mixture of $\text{W(CH}_2\text{SiMe}_3)_3(\equiv\text{CSiMe}_3)$ (1, 20.7 mg, 0.04 mmol), 4,4-dimethylphenyl (internal standard), and toluene-$d_8$ (ca. 0.65 mL) in a J.R. Youngs NMR tube was added a ca. 0.7–1.8 equiv PMe$_3$ via syringe. A weighed amount of 4,4-dimethylphenyl was used, and its concentration in the solution was typically in the 0.02–0.03 M range. The sample was kept at room temperature for 48 h to ensure that equilibrium was established. The NMR probe was pre-cooled or pre-heated to the set temperature. After the NMR tube was inserted into the probe, a $^1$H NMR spectrum was taken after the temperature was stabilized. $K_{eq1} = [4a]/([1] [\text{PMe}_3])$ were calculated from the integration of 1, PMe$_3$, and 4a. The Me peak in 4,4-dimethylphenyl, –CH$_2$– peak in 1, and the PMe$_3$ peak in 4a were used in the integration and calculation of $K_{eq1}$.

2.2. Thermodynamic study of the equilibrium between $\text{W(CH}_2\text{SiMe}_3)_3(\equiv\text{CSiMe}_3)$ (1), PMe$_2$Ph and the $3b = 4b$ tautomeric mixture

At least five experiments were conducted. A mixture of $\text{W(CH}_2\text{SiMe}_3)_3(\equiv\text{CSiMe}_3)$ (1, 29.1 mg, 0.06 mmol), 4,4-dimethylphenyl (internal standard), and toluene-$d_8$ (ca. 0.53 mL) in a J.R. Youngs NMR tube was added a ca. 1.0–1.5 equiv PMe$_2$Ph via syringe. A weighed amount of 4,4-dimethylphenyl was used, and its concentration in the solution was typically in the 0.02–0.03 M range. The sample was kept at room temperature for five days to ensure that equilibrium was established. The NMR probe was pre-cooled or pre-heated to the set temperature. After the NMR tube was inserted into the probe, the $^1$H NMR spectrum was taken after the temperature was stabilized. After the sample was placed at the set temperature for 30 min, no change in the NMR spectrum was observed. The sample was, however, kept for two hours at each temperature, during which NMR spectra were taken every 30 min to ensure no further change was observed. $K_{eq2} = [4b]/([1] [\text{PMe}_2\text{Ph}])$ were calculated from the integration of 1, PMe$_2$Ph, and 4b. The Me peak in 4,4-dimethylphenyl, –CH$_2$– peak in 1, Me peak in PMe$_2$Ph, and the PMe$_2$Ph peak in 4b were used in the integration and calculation of $K_{eq2}$.

2.3. Computational methods

All calculations were carried out using Gaussian 09 [15]. The performance of the density functional theory (DFT) methods B3LYP [16,17], M06 [18], and BP86 [19] has been examined. Triple-$\zeta$ basis sets 6–311G(d, p) [20–22] were used for H, C, Si, and P; and def2-TZVP [23,24] with effective core potentials (ECP) [25] were employed for tungsten. The basis set was found to be excellent in describing metal–carbon and metal–oxygen bonds [26,27]. Geometry optimizations and vibrational frequency calculations were performed both in gas phase and solution. Solvation effects were treated with the continuum solvent models SMD [28]. Thermal corrections are calculated at standard conditions (298.15 K and 1 atm).

3. Results and discussion

3.1. Thermodynamic study of the addition of PMe$_3$ to 1

Alkyl alkylidyne $\text{W(CH}_2\text{SiMe}_3)_3(\equiv\text{CSiMe}_3)$ (1) was treated with a various amount of PMe$_3$ (0.7–1.8 equiv) to probe the addition reaction of phosphine and the position of the equilibrium (Scheme 4). The addition was fast and essentially completed by the time NMR spectra were recorded. After the addition, the solution in toluene-$d_8$ was kept at room temperature for 48 h to ensure that equilibrium was established. Variable-temperature NMR spectra of the mixtures were studied, and the equilibrium constants, $K_{eq1} = [4a]/([1] [\text{PMe}_3])$, measured with a variable amount of PMe$_3$ between 273 and 303 K are listed in Table 1. The peaks of 3a were very small and ignored for the calculations of $K_{eq1}$. For the 3a = 4a tautomization, 4a dominates by a ratio of ca. 9.4–12.3 [6a,b]. A plot of ln $K_{eq1}$ versus 1000/$T$ (Fig. 1-Left) gave $\Delta H^\circ = 10.0$ (1.1) kcal mol$^{-1}$ and $\Delta S^\circ = -23(4)$ eu, indicating that the addition is exothermic. The large, negative entropy of the reaction is not surprising, as in the addition, two molecules give one adduct molecule. The equilibrium constants ($K_{eq1}$) range from 10.8 $\times$ 10$^2$ at 273 K to 1.7 $\times$ 10$^2$ at 303 K, indicating that the 3a = 4a tautomers are strongly favored. Hence, PMe$_3$ strongly binds to 1 and its dissociation is disfavored. At higher temperatures, the equilibrium shifts towards 1 + PMe$_3$.

3.2. Thermodynamic study of the addition of PMe$_2$Ph to 1

PMe$_2$Ph was utilized for comparison with PMe$_3$, W(CH$_2$SiMe$_3$)$_3$- (≡CSiMe$_3$) (1) in toluene-$d_8$ was added a various amount of ca. 1.0–1.5 equiv of PMe$_2$Ph via syringe. The addition to 1 is much slower than the one involving PMe$_3$, and takes about 2–3 days at room temperature to reach the equilibrium. The sample was kept at room temperature for 5 days to ensure that equilibrium was established.

$K_{eq2} = [4b]/([1] [\text{PMe}_2\text{Ph}])$ were calculated from the integration of 1, PMe$_2$Ph, and 4b. The Me peak in 4,4-dimethylphenyl, –CH$_2$– peak in 1, Me peak in PMe$_2$Ph, and the PMe$_2$Ph peak in 4b were used in the integration and calculation of $K_{eq2}$.

Please cite this article in press as: P. Chen et al., Polyhedron (2012), http://dx.doi.org/10.1016/j.poly.2012.07.042
Variable-temperature NMR spectra of the exchange of 1 and PMe2Ph with 3b/4b were studied, and the equilibrium constants, \(K_{eq1} = |4b|/|1| \text{ [PMe2Ph]}\), measured between 263 and 303 K with a variable amount of PMe2Ph are listed in Table 1. A plot of In \(K_{eq1}\) versus 1000/T (Fig. 1-Right) gave \(\Delta H^r = -3.0 \text{ (0.7) kcal mol}^{-1}\) and \(\Delta S^r = -6(3)\) eu. The equilibrium constants (\(K_{eq1}\)) range from 16.4(1.5) at 263 K to 7.5(0.5) at 303 K. The much smaller equilibrium constants, in comparison to those of addition of PMe2Ph to 1 (Table 1), suggest that, although the 3b = 4b tautomer and the bis-alkylidene (4b) are favored, the binding of PMe2Ph to 1 is not as strongly favored as the binding of PMe3. This is also reflected in smaller \(\Delta H^r\) and thus the release of much less energy during the addition of PMe2Ph to 1. The reaction entropy is also less negative. This is presumably due to the fact that PMe3 is a stronger \(\sigma\)-donor than PMe2Ph, and the steric involving more bulky phenyl group versus Me in PMe2 may also be a factor. With decreasing temperature, the equilibrium shifts towards 1. The 1 + PMe2Ph = 3b/4b equilibrium \([K_{eq1} = 16.4(1.5) \text{ at 273 K}]\) is shifted more to the left \((1 + \text{PMe2Ph})\) than the \(1 + \text{PMe3} = 3a/4a\) equilibrium \([K_{eq1} = 10.8(0.4) \times 10^7 \text{ at 273 K}]\).

3.3. Calculations – benchmarking

To evaluate the performance of computational methods, the thermodynamics of two processes, the equilibrium \(1 + \text{PMe3} = 4a\) and the equilibrium \(3a = 4a\), were calculated and compared with the experimentally measured values.

Relative enthalpies calculated using a series of DFT methods are listed in Table 2. All of the relative enthalpies \((\Delta H_1)\) of the equilibrium \(3a = 4a\) calculated at B3LYP, M06 and BP86 agree with the experimental measured value reasonably well [6a]. However, neither B3LYP nor BP86 level of theory can reproduce the reaction enthalpy of 1 and PMe3 \((\Delta H_1)\). Underestimation of binding energy by various DFT methods has been reported recently [29–33]. The \(\Delta H_1\) calculated by M06 is consistent with the experimental result. The experimental results \((1 + \text{PMe3} = 4a)\) identify M06 as an appropriate method for the system. Solvent effect does not affect the relative stabilities of 3a and 4a much, but decrease the binding enthalpies by ca. 4 kcal mol\(^{-1}\).

Overestimation of the entropy for the process which involves molarity change by gas-phase calculation is well-known [34–36]. This is due to the fact that translational and rotational degrees of freedom in gas phase are reduced in solution. Several approximations have been applied to account for this effect in different systems [37–39]. As shown in Table 3, the calculated entropy loss \(\Delta S_1 (56.1 \text{ eu})\) for the bimolecular process \((1 + \text{PMe3} = 4a)\) is significantly higher than the experimental value (–23 eu). This problem cannot be addressed by performing full optimization and frequency calculation in toluene with SMD. On the other extreme, one can estimate the entropy by neglecting the translational and rotational contribution but only taking the vibrational contribution into account [40]. However, this will underestimate the entropy simply because translation and rotation are in reality not completely suppressed. Therefore, one solution is to fit a scaling factor between 1 and 0 for the rotational and translational entropy contribution \((S_{\text{trans}} + S_{\text{rot}})\) to reproduce the experimental results. For the reaction studied here, a factor of 0.65 was found to be suitable for scaling the entropy in solution. The corrected entropy calculated by Eq. (3) (–22.8 eu) is closed to the experimental measured value (–23(4) eu).

\[
S_{\text{corr}} = 0.65 \times (S_{\text{trans}} + S_{\text{rot}}) + S_{\text{vib}}.
\]  

The M06/(6-311G(d, p), def2-TZVP with ECP) level of theory with SMD solvent corrections was chosen for the calculation in this work while the entropy values in the following discussion were corrected as outlined above.

3.4. Formation of 4: theoretical studies of the thermodynamics

The calculated values for \(1 + \text{PMe2} = 4a\) are consistent with the measured values (Table 4). The equilibrium favors 4a. In the case of PMe2Ph (4b), the free energy is close to 0 kcal mol\(^{-1}\), implying that the concentrations of 1 and 4 are comparable in the equilibrium mixture. The positive free energy of binding \(\Delta G_1\) and the significant longer W–P distances of 4c and 4d imply that such processes are unfavorable, agreeing well with the experimental observation that bulky PPh3 and PCy3 cannot form complexes 4.

![Fig. 4. Potential free energy surface for different tautomerization pathways with geometries of the transition states 1TS2, 3TS4-a, 3TS4-b (distances in Å, angles in degree, free energies in kcal mol\(^{-1}\)).](image-url)
The binding preference of PR₃ ligand with the alkylidyne (1) or bis(alkylidene) (2) have already been analyzed in a molecular orbital diagram [6a]. Here, we use an energy-decomposition analysis to probe the binding energy [41,42]. This strategy decomposes the binding energy into two parts, deformation energy and interaction energy. The deformation energy is the energy induced by the distortion of binding partners into the geometries adopted in the corresponding adduct. As shown in Fig. 2, the relative energies of 3a-frag and 4a-frag were calculated by summing the single point energy of the tungsten fragment and the PMe₃ fragment of 3a and 4a, respectively. The interaction energy is the inherent energy to separate two fragments. The interaction energy of ΔEₜₐₚₙ for 4a is higher than that for 3a, consistent with the previous MO analysis [6a]. The deformation energy for 2 is less than that of 1, reflecting the relative minor geometrical distortion of 2 to 4a compared to that of 1 to 3a.

3.5. Formation of 4: theoretical studies of the kinetics

After discussing the thermodynamics of the formation of 4 from 1 and PR₃, we turned to the mechanism and kinetics of this process. As shown in Scheme 4, the transformation of 1 + PR₃ to 4 may undergo two possible pathways, i.e., 1 → 2 → 4 or 1 → 3 → 4. The difference in the two pathways is a reversal of the sequence of ligand binding and tautomerization. It is hypothesized that the ligand binding is a fast step. To investigate the binding process, an energy surface scan along the W-P distance was carried out. Fig. 3 shows the relative energy (ΔEₜₐₚₙ) versus W-P distance. The association energy curves revealed that the PR₃ binding steps are indeed barrierless.

Theoretical studies then focused on the tautomerization of the α-H transfer, which will be the rate-determining step for the formation of 4. The structures and the free energy relative to reference (1 + PR₃) of transition states of 1TS2, 3TS4-a and 3TS4-b are shown in Fig. 4. 1TS2 adopts a tetrahedral geometry, while both of 3TS4-a and 3TS4-b have a trigonal bipyramidal geometry. Because the smaller distortion of 3TS4-a and 3TS4-b from their precursor intermediates, the free energy barriers for ligated tautomerization (3TS4-a: 28.1 kcal mol⁻¹ and 3TS4-b: 29.0 kcal mol⁻¹) are much lower than that of ligandless tautomerization (1TS2: 38.7 kcal mol⁻¹). Since the binding of PR₃ ligand is a barrierless process, it suggests that the formation of 4 undergoes the pathway along 1 → 3 → 4, instead of 1 → 2 → 4.

3.6. Transformation of 4 to the alkyl alkylidene alkylidyne complexes 5 and 6

As reported previously, heating the tautomeric equilibrium mixtures of 3 → 4 in the presence of phosphines leads to the interesting tungsten alkyl alkylidene alkylidyne complexes W(CH₂SiMe₃)(=CHSiMe₂)(=CSiMe₃)(PR₃)₂ (R₃ = Me₃, 5a: Me₂Ph, 5b) (Scheme 4) [6d]. The mechanism of the transformation of 4a,b to the tungsten alkyl alkylidene alkylidyne complexes is not clear. Therefore, DFT calculations have been performed here to explore the reaction pathways. As shown in Scheme 4, the 3a = 4a → 5a conversion includes two elementary steps, i.e., SiMe₄ elimination and binding of a second equivalent of PR₃. The previous experimental kinetics study suggests that SiMe₄ elimination occurs prior to the addition of a second PR₃. That allows us to focus on the step of SiMe₄ elimination.

The potential energy surface of the formation of 8a, which then binds PMe₃ to give the bisphosphine product 5a, from 1 is shown in Fig. 5. The coordination of the phosphine ligand PMe₃ and the equilibrium between 3a and 4a have been discussed above. 4a is a thermodynamically stable intermediate. At higher temperatures, 3a and 4a may undergo an α-H abstraction to eliminate SiMe₄ and give the monophosphine and alkyl alkylidene alkylidyne intermediate 8a. For 4TS6-a, the α-H transfer takes place from one alkyl group to another alkyl group, while the α-H transfer occurs from alkylidene to alkyl group in 4TS6-a. The relative free energy of
4TS6-a is 34.7 kcal mol⁻¹, 5.5 kcal mol⁻¹ higher than 3TS6-a, suggesting that the pathway 4a → 3a → 8a is more favorable for the formation of the tungsten alkyl alkylidyne alkylidyne complex 5a. The overall enthalpy and free energy barrier from 4a to 8a are calculated to be 32.2 and 31.2 kcal mol⁻¹, in a reasonable agreement with the experimental measured values (29 and 28 kcal mol⁻¹). The slightly higher barrier of transformation from 4a to 8a than that of the transformation from 1 to 4a, indicating that 4a is a kinetically stable intermediate.

4. Concluding remarks

Addition of two mono-dentate phosphines (PR₃ = PMe₃ and PMe₄Ph) to W(CH₂SiMe₃)₂(=SiMe₃)PR₃ (3a, 3b) and their bis-alkyltetraen W(CH₂SiMe₃)₂(=CHSiMe₃)₂(PR₃) (4a, 4b), has been found to be reversible. It should be noted that the reaction of excess W(CH₂SiMe₃)₃(=SiMe₃) (1) and Me₃PCH₂CH₂PMe₂ (DMPE) appears to be more complicated than the reaction of 1 with the mono-dentate phosphines, and is not pursued in the current work. Using a comparison with the experimental thermodynamic data, benchmarking work has been carried out and MO6 is found to be an appropriate method for this system. Consequently, a detailed computational study has been performed to investigate the reaction of W(CH₂SiMe₃)₂(=SiMe₃) (1) with PR₃. Because the binding of PR₃ ligand is barrierless and the PR₃ facilitates the α-H migration, the formation of 4 undergoes the pathway along 1 → 3 → 4, instead of 1 → 2 → 4. Heating the tautomeric equilibrium mixtures of 3 → 4 in the presence of the phosphine gives the tungsten alkyl alkylidyne alkylidyne complexes W(CH₂SiMe₃)₂(=CHSiMe₃)-PR₃ (PR₃ = PMe₃, 5a, PMe₄Ph, 5b). The potential energy surface of the formation of 8a indicates that the relative free energy of 4TS6-a is higher than 3TS6-a. This suggests the formation of 8a along the pathway 4a → 3a → 8a, followed by binding of 8a to PMe₃ to give the bishphosphine product 5a. This study provides a missing piece to understand the role of 4 plays along the pathway of the reaction of 1 and PR₃. 4 is found to be a thermodynamically and kinetically stable intermediate.

Acknowledgments

Financial support from the National Science Foundation of China (21133002), US National Science Foundation (CHE-1012173), the Shenzhen Peacock Program, and Peking University Shenzhen Graduate School is acknowledged. We would like to thank Prof. Olaf Wiest for helpful discussion and the Shenzhen Supercomputer Center for computational resources.

References


Please cite this article in press as: P. Chen et al., Polyhedron (2012), http://dx.doi.org/10.1016/j.poly.2012.07.042
[24] (a) The basis sets were obtained from the Gaussian Basis Set Library EMSL at
https://bse.pnl.gov/bse/portal.;